Indian J. Phys. **82 (1)** 117-121 (2008)

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Electronic spectral studies of 4-bromo-2-fluoro phenol in various solvents

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Received 22 November 2006, accepted 11 December 2006

Abstract : Electronic spectra of 4–bromo–2–fluoro phenol in polar solvents (ethanol, methanol and chloroform) have been recorded in liquid state in the region 200 to 400 nm The effect of halogen atom on the π-π^*, n-π^* and n-σ^* transitions have been studied The π-π^*, n-π^* and n-σ^* transitions have been shown the usual behavior towards the substitution and polarity of solvent. The effect of pH variation on electronic transitions of this compound in ethanol solvent has also been studied

Keywords : Ultraviolet absorption spectra, electronic absorption bands.

PACS No. : 33.20.Lg

Phenol has been the subject of numerous studies, since it is a good model for the investigation of hydrogen bonding and proton transfer in enzymes. Recent spectral investigation on halogen phenols find interesting application in agriculture and pharmacy. Solvent effect on electronic absorption spectra of halogen derivatives have been studied by many workers [1–3]. Experimentally some workers [4,5] have found evidence of the presence of electronic transitions other than n-π^* and π-π^* in the spectra of halogen derivatives of phenol and aniline and on substitution n-π^* and π-π^* system of phenol produce bathochromic (red) shift and hypsochromic (blue) shift respectively. But no work appears to have been carried out on the ultraviolet absorption spectra of 4-bromo-2-fluoro phenol. The present paper reports the solvent effect on the electronic spectra of the said compound. The effect of pH variation has also been discussed on the electronic transitions of the said compound.

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The spec-pure compound 4-bromo-2-fluoro phenol was obtained from M/s Aldrich Chemie, West Germany used for spectral studies Its purity was confirmed by elemental analysis and melting point determination The ultraviolet spectra of the said compound were recorded in solvents (ethanol, methanol and chloroform) on UV-VIS double beam spectro-photometer, Model M-1601 in the region of 200–400 nm in liquid state The solvents used for preparing the solution of the compound were of spectroscopic grade The pH value of solution was measured with Systronic pH digital meter (Model 335) This system was standardized at pH 4 ± 0 1, 7 ± 0 1, 9 ± 0 1 at room temperature with the help of standard buffers The concentration of the solution in all cases was kept constant (8×10^{-3} gm/litre) The ratio of pure solvent and acid or alkali was maintained at 9 1 by volume

The molecular structure of 4-bromo-2-fluoro phenol are shown in Figure 1 The effect of solvents on the electronic transitions of this compound is given in Table 1 The effect of pH variation in solvent ethanol on the electronic transitions of this compound is given in Table 2 The near ultra-violet absorption spectra of this compound are shown in Figure 2 The absorption spectra of this molecule in ethanol solvent at different pH is shown in Figure 3

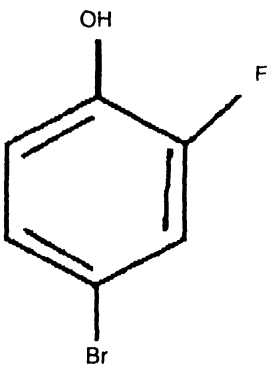

Figure 1. Molecular structure of 4-bromo-2-fluoro phenol

Table 1. Effect of solvents on electronic transition of 4-bromo-2-fluoro phenol (all values are in mm)

Solvent	*RI*	DC	n-π^*	π-π^*	n-σ^*
Ethanol	1 3773	25	287	–	209
Methanol	1 3662	32 5	279	224	206
Chloroform	1 458	4 5	279	241	203

RI = Refractive index, DC = Dielectric constant

Effect of substitution and solvent polarity on electronic transition :

In phenol a band observed at 230–245 nm corresponds to $A_1 \rightarrow B_2$ transition and is derived from $A_{1g} \rightarrow B_{2u}$ transition on lowering the symmetry from $D_{6h} \rightarrow C_{2v}$.

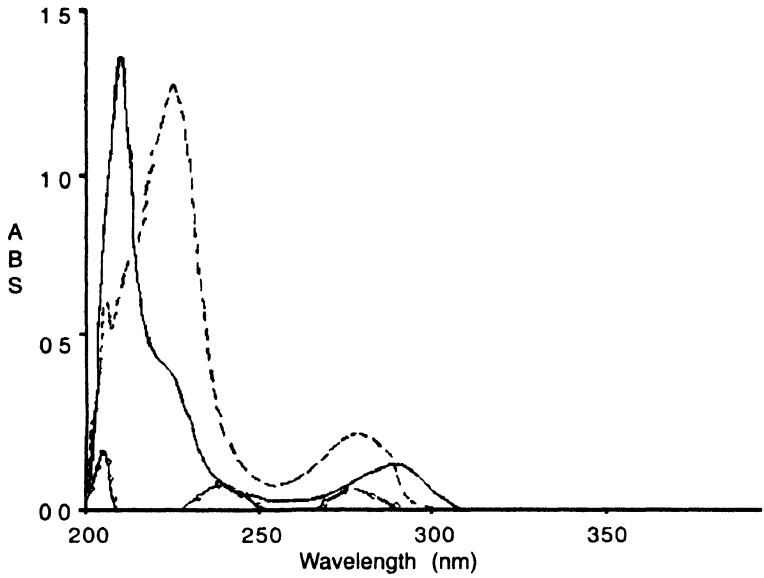

Figure 2. Ultraviolet absorption spectra of 4-bromo-2-fluoro phenol in ethanol (—), methanol ( ) and chloroform (–0–)

Table 2. Effect of pH variation on electronic transition of 4-bromo-2-fluoro phenol (all values are in mm)

Solvent	*RI*	pH value	n-π^*	π-π^*	n-σ^*
Ethanol	1 3773	8 76	287	-	209
Ethanol + HCl		3 90	280	225	209
Ethanol + NaOH		11 98	297	244	209

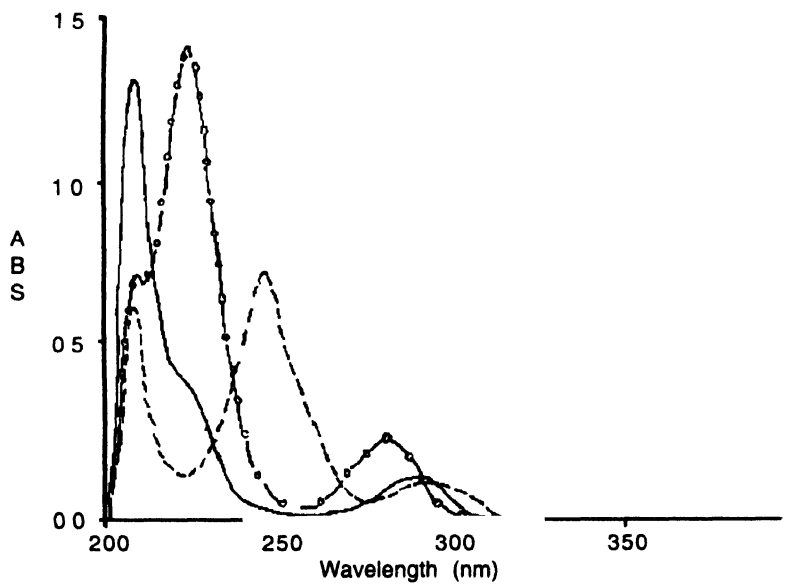

Figure 3. Ultraviolet absorption spectra of 4-bromo-2-fluoro phenol in ethanol (—), neutral ( ) acid and (–0–) alkaline medium.

Jeegagal and Rao [6] suggested that 210 nm and 220 nm bands of trisubstituted benzene corresponds to $A_{1g} \rightarrow B_{1u}$ and $A_{1g} \rightarrow E_{1u}$ transitions of benzene. Goyal and Gupta [7] have calculated the electronic transition n-π^* corresponds to out of plane transition π-π^* and n-σ^* transitions inplane transitions.

According to Silverstein [8] the molecules containing non bonding electron substituents, there occur a band around 280 nm which corresponds to n-π^* transition, band 200–215 nm corresponds to n-σ^* transitions.

The emergence of n-π^* transition only in hydrogen bonding solvent is due to the increase in excitation energy. The hydrogen bonding which stabilized the ground state will be weakened by the shift of electron density away from the non bonding centre on excitation, with a consequent increase in the excitation energy and appearance of a blue shift. The higher the polarity of the solvent greater will be the amount of solvation. However solvation may be partly due to hydrogen bonding of solvent (if protonic) with solute [9]. Methanol being more polar and protonic than ethanol, is stronger hydrogen bonding solvent. This explains very well the blue shift of n-π^* bands observed in 4-bromo-2-fluoro phenol on increasing the polarity of solvent (ethanol → methanol → chloroform) given in Table 1 which agrees with the literature values [10,12].

For n-σ^* transition the ground state is more stabilized than exited states and absorption shifts to shorter wavelength and the blue shift increases as the solvent polarity increases [9]. The band position may be much influenced by other factors such as hydrogen bonding. The shift in hydrogen bond may be explained on the basis of solution energies of solute which includes induced dipole-dipole forces between non polar solvent and polar solvents [13]. According to Jagmohan [13], on excitation of the localized non bonding electron is delocalized on the less electronegative atoms over which the exited orbital (π^* or σ^*) is reduced in the exited state. In present study the blue shift in n-σ^* transition is observed in 4-bromo-2-fluoro phenol on increasing the polarity of solvents (ethanol → methanol → chloroform) given in Table 1 which is similar to the behaviour observed in literature [11,12,14].

For π-π^* transition both ground state and exited stated are stabilised and absorption moves to longer wavelengths. The π-π^* transition undergoes a red shift with increasing the polarity of solvents (ethanol → methanol → chloroform) [8,9]. This can be attributed to the monetary polarization of the solvents by transition dipole of solute. From Table 1 it is evident that red shift is observed in the π-π^* transitions of 4-bromo-2-fluoro phenol on increasing the polarity of solvents (ethanol → methanol → chloroform) which is in good agreement with literature values [10–17].

Effect of pH variation :

Since the interpretation of spectral measurement to a considerable extent mainly depend on the choice of sites of localized of protons, the question of possible effect

of pH variation on electronic transition of the said compound under study is very important.

In case of dichloro-nitro-aniline there is a blue shift in the position of entire band with decrease in pH, the n-π^* and π-π^* bands shifted towards shorter wavelength in the acidic solution by many workers [14]. Kalsi [9] have suggested a blue shift of n-system in strong acidic solution due to the binding of non bonded electrons by protonation. In accordance with the above, we have also observed a blue shift in n-π^* and π-π^* bands with the addition of acid in the aqueos solution of 4-bromo-2-fluoro phenol as the neutral form changes to acidic form *i.e.* with the increase in pH value a red shift is observed in the n-π^* and π-π^* bands of the said molecule is given in Table 2. This is in good agreement with literature value [10–14].

Acknowledgment

Authors are highly grateful to Shri Abdul Hak, Head Technician, IIT Roorkee for arranging necessary facilities for testing and fruitful guidance.

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